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Electronic polarizabilities of ions in polymers of alkali-halides

R S Chauhan

Department of Physics, R B S College, Agra-282 002, Uttar Pradesh, India

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Abstract : In the present paper, we report the values of electronic polarizabilities of alkali and halogen ions-calculated in the bonded state by taking the effect of Coulomb potential into account within the framework of Seitz-Ruffa energy level model. We have considered all the monomers, dimers, trimers and tetramers as well as crystals of alkali halides. The Coulomb potentials at different ion-sites are calculated by considering different possible geometrical structures for the polymers under study. It is found that the electronic polarizabilities of ions are significantly modified in the bonded state as compared to the free state values. It is emphasized that the bonded state polarizabilities are more appropriate for predicting the dipole moments and can further be used in studying the properties of polymers

Keywords : Electronic polarizabilities, molecules and crystals of alkali-halides, Coulomb potentials

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1. Introduction

The electronic polarizabilities of ions are the quantities of fundamental interest and used as basic input data for studying various properties of polymers such as binding energy, dipole moments and spectroscopic constants [1–5]. In the original Rittner model [1], properties of alkali halide monomers were calculated using Pauling's free ion values of electronic polarizabilities [6]. However, it has been emphasized by subsequent workers [7–11] that the Pauling's free state polarizabilities are not appropriate for calculating the bonded state properties. In fact, the electronic polarizability of cations increases and that of anions decreases in the bonded state as compared to the corresponding values in the free state. These enhancement and reduction in the values of electronic polarizabilities of cations and anions respectively arise mainly due to the existence of Coulomb potential which is negative at cation sites and positive at anion sites. The effect of Coulomb potentials on electronic polarizabilities can be estimated quantitatively using the model developed by Seitz [12] and Ruffa [7] on the basis of energy level analysis.

In the present study, we consider all the monomers, dimers, trimers and tetramers of alkali halides. First we calculate the magnitudes of Coulomb potentials at different ion sites in these polymers using the appropriate geometrical structures as suggested by Ramondo *et al* [13]. Then we estimate the effect of these Coulomb potentials on the electronic polarizabilities of ions in all the polymers of alkali halides, The method of analysis is presented in Section 2. The results are reported and discussed in Section 3.

2. Method of analysis

According to the Seitz-Ruffa (SR) energy level analysis, the polarizabilities of ions in molecules differ from the corresponding free state values because of the existence of Coulomb potential which is negative at the cation site and positive at the anion site. Electronic polarizability of an ion in the free state α_f has been related to an effective energy parameter E_f by Rutfa [7] using the Quadratic Stark effect and the Thomas-Kuhn sum rule. The resulting formula is expressed as follows :

$$\alpha_f = \frac{e^2h^2n}{4\pi^2mE_f^2}. \tag{1}$$

Here e and m are the charge and mass of the electron respectively. n is the total number of electrons in the ion, h is the Planck's constant. Taking the values of α_f from Pauling [6], E_f are calculated and reported in Table 1 alongwith input data. The molecular state

Table 1 Values of free ion polarizabilities α_f(Å^3), number of electrons and energy parameter $E_f(eV)$.

Ion	α_f Pauling [6]	n	E_f
Li^+	0.029	2	86.86
Na^+	0.18	10	77.91
K^+	0.83	18	48.67
Rb^+	1.40	36	53.00
Cs^+	2 40	54	49.37
F^-	1 04	10	32 41
Cl^-	3.66	18	23 18
Br^-	4.77	36	28.71
I^-	7.10	54	28.83

polarizability α_1 for cation and α_2 for anion are then estimated using the following expressions :

$$\alpha_1 = \frac{e^2h^2n}{4\pi^2m(E_f - e\phi_c^+)^2}, \tag{2}$$

and

$$\alpha_2 = \frac{e^2h^2n}{4\pi^2m(E_f + e\phi_c^-)^2}, \tag{3}$$

where ϕ_c^+ and ϕ_c are the magnitudes of Coulomb potentials at cation sites and anion sites respectively.

In order to estimate the values of ϕ_c^+ and ϕ_c^-, we consider the geometrical arrangements for the polymers under study as shown in Figure 1. For monomers, dimers and trimers there is only one possible structure for each corresponding to their stable configurations [14,15]. For tetramers, however, there are two possible structures as suggested by Ramondo *et al* [13]. The interionic distances corresponding to various structures are given in Tables 2, 3 and 4. Using these values of ionic separations, we now estimate ϕ_c^+ and ϕ_c^- with the help of the following expressions :

FIGURE 1 (a-e)

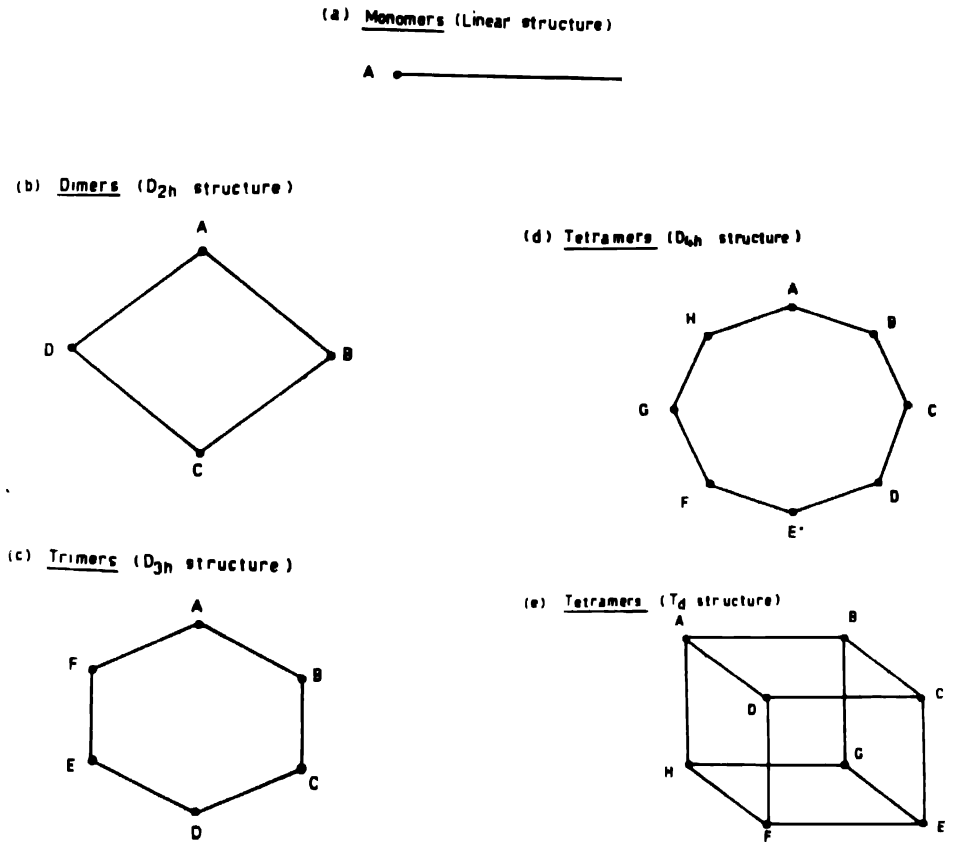

Figure 1(a). Here A is cation and B is anion and hence separation between cation A and anion B is AB = $r_{+\,-}$. (b) Here A and C are cations, B and D are anions Hence AB = BC = CD = DA = $r_{+\,-}$, AC = r_{++}, and BD = $r_{-\,-}$. (c) Here A, C, E are cations and B, D, F are anions. Hence AB = BC = CD = EF = FA = $r_{+\,-}$, AC = AE = r_{++}, DF = DB = $r_{-\,-}$, and AD = $r'_{+\,-}$ (second neighbour separation between cations & anions).

Figure 1(d). Here A, C, E, G are cations and B, D, F, H are anions. Hence AB = BC = CD = DE = EF = FG = GH = HA = $r_{+\,-}$, AC = CE = EG = GA = r_{++}, BD = DF = FH = HB = $r_{-\,-}$, AE = CG = r'_{++} and BF = DH = $r'_{-\,-}$. (e) Here A, C, E, G are cations and B, D, F, H are anions. Hence AB = BC = CD = EF = GH = FH = $r_{+\,-}$.

Table 2. Valuesof interionic distances (in nm).

Monomers MX	r_{+-}	Dimers M_2X_2	r_{+-}	r_{++}	r_{--}
LiF	0.156	Li_2F_2	0.170	0.210	0.269
LiCl	0.202	Li_2Cl_2	0.226	0.270	0.362
LiBr	0.217	Li_2Br_2	0.237	0.275	0.387
LiI	0.239	Li_2I_2	0.257	0.278	0.433
NaF	0.193	Na_2F_2	0.205	0.277	0.301
NaCl	0.236	Na_2Cl_2	0.265	0.316	0.426
NaBr	0.250	Na_2Br_2	0.277	0.324	0.448
NaI	0.271	Na_2I_2	0.295	0.330	0.489
KF	0.217	K_2F_2	0.224	0.320	0.313
KCl	0.267	K_2Cl_2	0.295	0.382	0.449
KBr	0.282	K_2Br_2	0.310	0.394	0.477
KI	0.305	K_2I_2	0.330	0.405	0.522
RbF	0.227	Rb_2F_2	0.246	0.359	0.338
RbCl	0.279	Rb_2Cl_2	0 302	0.405	0.448
RbBr	0.295	Rb_2Br_2	0.317	0.415	0.480
RbI	0.318	Rb_2I_2	0.342	0 429	0.531
CsF	0.235	Cs_2F_2	0.255	0.387	0.332
CsCl	0.291	Cs_2Cl_2	0.319	0.442	0 461
CsBr	0.307	Cs_2Br_2	0.332	0.443	0.494
CsI	0.332	Cs_2I_2	0.356	0.459	0.545

Table 3. Values of interionic distances (in nm).

Trimers	r_{+-}	r_{++}	r_{--}	r'_{+-}
Li_3F_3	0.180	0.280	0.335	0.353
Li_3Cl_3	0.227	0.335	0.433	0.443
Li_3Br_3	0.245	0.358	0.469	0.478
Li_3I_3	0.266	0.363	0.518	0.508
Na_3F_3	0.214	0.350	0 388	0.426
Na_3Cl_3	0.257	0.391	0.484	0.505
Na_3Br_3	0.272	0.404	0.517	0.532
Na_3I_3	0.294	0.412	0.569	0.566
K_3F_3	0.245	0.431	0.420	0.494
K_3Cl_3	0 294	0.482	0.533	0.586
K_3Br_3	0.311	0.493	0.575	0.617
K_3I_3	0.332	0.497	0.630	0.651

Table 3. *(Cont'd.)*.

Trimers	r_{+-}	r_{++}	r_{--}	r'_{+-}
Rb_3F_3	0.258	0.464	0.428	0.515
Rb_3Cl_3	0.309	0.521	0.548	0.617
Rb_3Br_3	0.325	0.529	0.592	0.648
Rb_3I_3	0.348	0.541	0.650	0.688
Cs_3F_3	0.271	0.506	0.424	0.539
Cs_3Cl_3	0.325	0.568	0.557	0.640
Cs_3Br_3	0.339	0.575	0.599	0.678
Cs_3I_3	0.367	0.594	0.671	0.730

Table 4. Values of interionic distances (in nm).

Tetramers	r_{+-}	r_{++}	r_{--}	r'_{++}	r'_{--}	r'_{+-}
Li_4F_4	0.180	0.302	0.352	0.427	0.498	0.428
Li_4Cl_4	0.227	0.358	0.451	0.506	0.638	0.529
Li_4Br_4	0.244	0.400	0.486	0.613	0.745	0.598
Li_4I_4	0.265	0.391	0.530	0.553	0.750	0.603
Na_4F_4	0.214	0.378	0.409	0.535	0.579	0.514
Na_4Cl_4	0.258	0.433	0.507	0.628	0.736	0.621
Na_4Br_4	0.272	0.429	0.540	0.607	0.764	0.634
Na_4I_4	0.294	0.450	0.586	0.636	0.829	0.678
K_4F_4	0.235	0.428	0.440	0.605	0.622	0.567
K_4Cl_4	0.296	0.523	0.566	0.740	0.800	0.712
K_4Br_4	0.311	0.530	0.605	0.750	0.856	0.742
K_4I_4	0.334	0.544	0.659	0.769	0.932	0.787
Rb_4F_4	0.246	0.459	0.449	0.649	0.635	0.593
Rb_4Cl_4	0.310	0.560	0.584	0.792	0.826	0.748
Rb_4Br_4	0.327	0.575	0.627	0.814	0.887	0.786
Rb_4I_4	0.351	0.592	0.685	0.837	0.969	0.835
Cs_4F_4	0.272	0.534	0.451	0.755	0.638	0.644
Cs_4Cl_4	0.327	0.611	0.598	0.864	0.846	0.790
Cs_4Br_4	0.342	0.620	0.643	0.877	0.909	0.825
Cs_4I_4	0.369	0.646	0.709	0.914	1.00	0.886

(a) For monomers (linear structure) :

$$\phi_c^+ = \phi_c^- = \frac{e}{r_{+-}}, \tag{4}$$

where r_{+-} is the separation between cations and anions.

(b) For dimers (D_{2h} structure) :

$$\phi_c^+ = \frac{2e}{r_{+-}} - \frac{e}{r_{++}} \tag{5}$$

and

$$\phi_c^- = \frac{2e}{r_{+-}} - \frac{e}{r_{--}}, \tag{6}$$

where r_{++} and r_{--} are the intercationic and interanionic separations respectively.

(c) For trimers (D_{3h} structure) :

$$\phi_c^+ = \frac{2e}{r_{+-}} + \frac{e}{r'_{+-}} - \frac{2e}{r_{++}} \tag{7}$$

and

$$\phi_c^- = \frac{2e}{r_{+-}} + \frac{e}{r'_{+-}} - \frac{2e}{r_{--}}, \tag{8}$$

where r'_{+-} is the second neighbour separation between cations and anions.

(d) For tetramers (D_{4h} structure) :

$$\phi_c^+ = \frac{2e}{r_{+-}} + \frac{2e}{r'_{+-}} - \frac{2e}{r_{++}} - \frac{e}{r'_{++}} \tag{9}$$

and

$$\phi_c^- = \frac{2e}{r_{+-}} + \frac{2e}{r'_{+-}} - \frac{2e}{r_{--}} - \frac{e}{r'_{--}}, \tag{10}$$

where r'_{++} and r'_{--} are the second neighbour intercationic and interanionic separations respectively.

(e) For tetramers (T_d structure) :

This structure represents the most simple cubic arrangement.

$$\phi_c^+ = \frac{3e}{r_{+-}} + \frac{e}{r'_{+-}} - \frac{3e}{r_{++}} \tag{11}$$

and

$$\phi_c^- = \frac{3e}{r_{+-}} + \frac{e}{r'_{+-}} - \frac{3e}{r_{--}}. \tag{12}$$

Here $r_{++} = r_{--} = r_{+-}\sqrt{2}$

and $r'_{+-} = r_{+-}\sqrt{3}$.

Hence $\phi_c^+ = \phi_c^-$.

After estimating the magnitudes of ϕ_c^+ and ϕ_c^-, we have calculated the molecular state polarizabilities α_1 and α_2 using eqs. (2) and (3).

(f) For crystals :

It is also interesting to calculate the values of polarizabilities in actual crystals where the potentials effective at ion sites are determined using the lattice sums following the method

of Madelung as described by Tosi [16]. Using this method and Ruffa's theory [7] the expressions for cation and anion polarizabilities (α_c^+ and α_c^-) are obtained as follows :

$$\alpha_c^+ = \frac{\alpha_f^+ (E_f^+)^2}{(E_f^+ - eV_M)^2}, \tag{13}$$

where V_M is the Madelung potential

and

$$\alpha_c^- = \frac{\alpha_f^- (E_f^-)^2}{\left[\frac{1}{4}\left\{\left(\Delta - e^2/r_0\right) + 3\left(E_f^- + \Delta - E\right)\right\}\right]^2}, \tag{14}$$

where

$$\Delta = 2e(V_M - V_R) + E - I + Qa.$$

Here, eV_M and eV_R are the Madelung and repulsive energies, respectively, E is the electron affinity of the halogen atom, I is the ionization potential of the alkali atom and Qa is the energy of interaction between the free atoms and the crystal environment. α_f and E_f are given by eq. (1). The calculated values of α_c^+ and α_c^- for alkali halide crystals are included in Tables 5 and 6.

Table 5. Calculated values of molecular state polarizabilities α_1 of alkali ions in (Å^3)

Alkali halides	(a) Monomer	(b) Dimer	(c) Trimer	Tetramer		Crystals
				(d) D_{4h}	(e) T_d	
LiF	0.036	0.037	0.037	0.037	0 038	0 043
LiCl	0.034	0.034	0.035	0.035	0 036	0 042
LiBr	0.034	0.034	0 034	0.035	0.035	0 041
LiI	0.033	0 033	0.033	0 033	0.035	0 040
NaF	0 220	0.227	0.229	0.230	0 234	0 252
NaCl	0.212	0.215	0.217	0.218	0 223	0.234
NaBr	0.210	0.212	0.214	0.216	0.223	0.232
NaI	0 208	0.208	0.209	0.209	0.217	0.220
KF	1.11	1.19	1.20	1.21	1.21	1.29
KCl	1.05	1 09	1 10	1.11	1 13	1 21
KBr	1.04	1.07	1.08	1.08	1.11	1 18
KI	1.02	1.04	1.04	1.04	1 09	1.16
RbF	1.81	1.93	1.94	1.96	1.93	2 04
RbCl	1.72	1.76	1.80	1.81	1.84	1 93
RbBr	1.70	1.75	1.77	1.77	1.81	1.90
RbI	1.67	1.72	1.72	1.73	1.78	1 86
CsF	3.16	3.38	3.41	3 43	3.36	3 56
CsCl	2.99	3.14	3.17	3.17	3.20	3.34
CsBr	2.95	3.08	3.10	3.11	3.16	3.32
CsI	2.91	3.00	3.02	3.02	3.09	3.25

Table 6. Calculated values of molecular state polarizabilities α_2 of halogen ions in (Å^3).

Alkali halides	(a) Monomer	(b) Dimer	(c) Trimer	Tetramer		Crystals
				(d) D_{4h}	(e) T_d	
LiF	0.632	0.582	0.571	0.567	0.589	0.691
LiCl	2.15	1.90	1.88	1.86	1.97	2.44
LiBr	3.15	2.84	2.84	2.82	2.96	3.93
LiI	4.86	4.38	4.34	4.31	4.58	6.38
NaF	0.688	0.642	0.629	0.626	0.633	0.772
NaCl	2.30	2.08	2.02	2.02	2.08	2.64
NaBr	3.31	3.04	2.99	2.95	3.07	4.19
NaI	5.06	4.64	4.56	4.53	4.73	6.64
KF	0.718	0.690	0.680	0.659	0.670	0.843
KCl	2.42	2.24	2.20	2.19	2.20	2.74
KBr	3.44	3.22	3.18	3.16	3.20	4.31
KI	5.24	4.89	4.81	4.80	4.90	6.74
RbF	0.729	0.709	0.700	0.678	0.684	0.873
RbCl	2.46	2.30	2.26	2.25	2.24	2.80
RbBr	3.49	3.28	3.25	3.24	3.25	4.37
RbI	5.31	4.97	4.92	4.91	4.96	6.87
CsF	0.736	0.733	0.727	0.703	0.698	0.899
CsCl	2.49	2.37	2.34	2.34	2.29	2.94
CsBr	3.53	3.36	3.33	3.32	3.29	4.43
CsI	5.37	5.08	5.04	5.03	5.03	6.96

The polarizabilities can be used to predict the dipole moments using the following Rittner and *T*-Rittner models.

$$\mu = er - \left[\frac{r^4 e(\alpha_1 + \alpha_2) - 4re\alpha_1\alpha_2}{r^6 - 4\alpha_1\alpha_2}\right] \tag{15}$$

and

$$\mu = er - \frac{e(\alpha_1 + \alpha_2)}{r^2}. \tag{16}$$

Eq. (16) has been found to compare well with the more rigorous quantum mechanical treatment [17]. Values of dipole moments (μ) calculated using eqs. (15) and (16) are reported in Table 7 and compared with other estimates.

Table 7. Calculated values of dipole moments μ in (Debye).

Molecule	(a)	(b)	(c)	(d)
LiF	7.511	5.410	6.196	6.284
LiCl	9.706	5.366	7.134	7.085
LiBr	10.422	5.524	7.170	7.226
LiI	11.488	5.510	7.377	7.429

Table 7. *(Cont'd.).*

Molecule	(a)	(b)	(c)	(d)
NaF	9.250	7.666	8.070	8.123
NaCl	11.339	8.026	9.170	8.972
NaBr	12.017	8.214	9.310	9.092
NaI	13.020	8.258	9.572	9.210
KF	10.432	8.523	8.566	8.558
KCl	12.809	9.772	10 460	10.238
KBr	13.549	10 163	10.839	10.603
KI	14.639	10.533	11.396	11.050
RbF	10.902	8.623	8 530	8.513
RbCl	13.385	10 251	10.795	10.483
RbBr	14.144	10 721	11.264	–
RbI	15.259	11 207	11 930	–
CsF	11.263	8 253	7.855	7 849
CsCl	13.957	10.504	10.834	10.358
CsBr	14.754	11.099	11.450	
CsI	15.921	11.762	12.295	12.100

(a) Point ion Model. (b) Rittner model using Pauling's free state polarizabilities.

(c) Present study. (d) Experimental [16].

3. Results and discussions

The bonded state electronic polarizabilities of ions in different polymers calculated in the present study using the method described in the preceding section, are reported in Tables 5 and 6. It is found that the calculated values in the bonded state are significantly different than the corresponding values of free state polarizabilities. The electronic polarizabilities of cations are increased and those of anions are decreased in the bonded state relative to free state. For a given cation the electronic polarizability increases from monomer-dimer-trimer-tetramer. In each polymer series, the polarizability of given cation decreases in the sequence of flourides-chlorides-bromides-iodides. For a given anion, the electronic polarizability decereases from monomer-dimer-trimer-tetramer. In each polymer series, the polarizability of a given anion increases in the sequence of Lithium-Sodium-Potassium-Rubidium-Cesium. The polarizabilities of cations increase and those of anions decrease in going from free state to the crystalline state. The polarizabilities in actual crystals are higher for cations as well as for anions than the corresponding polarizabilities in monomers and polymers. The crystalline state polarizability for a given cation decrease in the sequence of flourides-chlorides-bromides-iodides, and for a given anion it increases in the sequence of Lithium-Sodium-Potassium-Rubidium-Cesium. This behaviour is similar to that observed for cation and anion polarizabilities in monomers and polymers.

In order to judge the suitability of the bonded state electronic polarizabilities calculated in the present study, we make use of them to predict the dipole moments and compare their values with the experimental data. Such a comparison is presented in Table 7 where we have also included the values of dipole moments based on point ion model and Pauling's free state polarizabilities alongwith experimental values of dipole moments. It is found that the values of dipole moments calculated using our bonded state polarizabilities present the best agreement with experimental data. This demonstrates the validity and usefulness of the polarizability data obtained in the present study.

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